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(54) Process for the production of hydrocarbons with a high octane number by the selective dimerization of isobutene

(57) A process is described for the production of hydrocarbons with a high octane number starting from hydrocarbon cuts containing isobutene by selective dimerization with acid catalysts, characterized in that the dimerization reaction is carried out in the presence of tertiary alcohols, alkyl ethers and primary alcohols in such a quantity as to have, in the feeding, a molar ratio tertiary alcohols + alkyl ethers + primary alcohols/isobutene higher than 0.1, a molar ratio tertiary alcohols/isobutene lower than 0.2 and a molar ratio primary alcohols/isobutene lower than 0.2, preferably operating at a reaction temperature ranging from 30 to 120°C, at a pressure lower than 5 MPa and feeding space velocities of less than 30 h^{-1}.

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D scription

[0001] The pr sent invention relates to a process for the production of hydrocarbons with a high octane number, obtained by the selective dimerization reaction of isobutene contained in hydrocarbon cuts and to a lesser degree of possible linear butenes, in the presence of moderate quantities of tertiary alcohols and alkyl ethers, which favour the production of higher selectivities on the part of the catalyst. The mixture obtained can then be hydrogenated with the conventional methods to obtain a product with further improved octane characteristics.

[0002] For reasons of an environmental nature, the composition of gasolines is being reformulated to obtain fuels which burn better and have fewer evaporative emissions.

[0003] In order to be able to reach this objective, it is necessary to reduce the content of aromatic compounds (mainly benzene), light olefins (photo-chemically reactive and precursors responsible for the formation of atmospheric ozone), sulfur and also the volatility (to minimize losses) and end boiling point of the gasolines.

[0004] All these measurements cause a contraction in the volume and a lack in the octane number of the new gasolines, making it necessary, on the basis of the present uncertainty regarding the use of alkyl ethers in fuels (Europ. Chem. News, 10-16 May 1999), to make more and more use of purely hydrocarbon compounds such as, for example, the alkylate.

[0005] These products are capable of positively contributing to the above demands as they have a high octane number (both the Research Octane Number (RON) and the Motor Octane Number (MON) are high), excellent boiling point properties (limited volatility but low end point) and they are practically without olefins and aromatics.

[0006] At present the alkylate is obtained by the reaction, in liquid phase, between isoparaffinic hydrocarbons, such as for example isobutane, and olefins, for example propylene, butenes, pentenes and relative mixtures, in the presence of an acid catalyst for the production of C_7-C_9 hydrocarbons with a high octane number to be used in gasolines (see for example: A. Corma, A. Martinez, Catal. Rev. - Sci. Eng., 35, (1993), 483 and references contained therein).

[0007] The main problem of the alkylation process is due to the fact that with an increase in regulations of an environmental nature, both traditional processes (with hydrofluoric acid and with sulfuric acid) are coming up against great difficulties, making the future uncertain: the process with hydrofluoric acid owing to the toxicity of this acid, especially in populated areas, and the process with sulfuric acid owing to the large production of acid mud as well as the extremely corrosive power of the catalyst.

[0008] Alternative processes with solid acid catalysts are being developed, but their commercial applicability has yet to be demonstrated.

[0009] An alternative process in refining for obtaining products with characteristics similar to the alkylate, can be offered by the hydrogenation of the so-called "polymer" gasoline.

[0010] The oligomerization process (often erroneously called polymerization in the field of refining) was widely used in the years 1930-1940 to convert low-boiling C_3-C_4 olefins into gasolines. The process produces a gasoline with a high octane number (RON about 97) but with a high sensitivity owing to the purely olefinic nature of the product (for more specific details on the process see: J.H. Gary, G.E. Handwerk, "Petroleum Refining: Technology and Economics", 3rd Ed., M. Dekker, New York, (1994), 250).

[0011] Typical olefins which are oligomerized are mainly propylene, which gives slightly higher dimers or oligomers depending on the process used, and isobutene which mainly gives dimers but always accompanied by considerable quantities of higher oligomers.

[0012] If we limit our attention to the oligomerization of isobutene, it is known that this reaction can be carried out either in batch, semi-continuous or in continuous, in both gas-solid phase and in liquid phase, generally at temperatures ranging from 50 to 300°C and at atmospheric pressure or at such pressures as to keep the reagents in liquid phase, if considered necessary.

[0013] Typical catalysts for the industrial oligomerization process of isobutene are phosphoric acid, generally supported on a solid (for example kieselguhr), or cationic exchange acid resins. The latter enable the use of blander temperature and pressure conditions, with respect to supported phosphoric acid (100°C and 1-2 Mpa vs 200-220°C and 3-10 Mpa).

[0014] Other catalysts have also been claimed in literature, both liquid acids such as H_2SO_4 or sulfonic acid derivatives, or solid acids such as, for example, silicoaluminas, mixed oxides, zeolites, fluorinated or chlorinated aluminas, etc.; none of these catalysts however have as yet allowed the set up of an industrial process such as that of supported phosphoric acid (F. Asinger, "Mono-olefins: Chemistry and Technology", Pergamon Press, Oxford, pages 435-456) and that of cationic resins (G. Scharfe, Hydrocarbon Proc., April 1973, 171).

[0015] From the product point of view, the main problem of this process lies in the fact that, in the oligomerization phase, heavy oligomers of isobutene such as trimers (selectivity of 15-30%) and tetramers (selectivity of 1-2%), are produced in excessive percentages. Tetramers are not at all within the gasoline fraction as they are too high-boiling and consequently represent a net loss in yield to gasoline; as far as trimers are concerned (or their hydrogenated derivatives), their concentration should be greatly reduced as their boiling point (170-180°C) is at the limit of future specifica-